A

Thesis

On

Fabrication and Characterization of Metal Organic Framework (MOF) Based Membrane

Submitted By

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CERTIFICATE

*This is to certify that the thesis entitled, "**Fabrication and Characterization of Metal Organic Framework (MOF) Based Membrane**" submitted by Rashmi Prava Mohanty in partial fulfillments for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.*

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ABSTRACT

Membrane-based separation is an increasingly viable, cost-effective complementary separation technology to traditional unit operation for a number of industrially important applications. MOFs as membrane materials are of particular interest for continuous membrane based separations, and other applications. Despite a great deal of research in MOFs as membranes, there still exist some challenges to fabricate continuous crack-free MOF membranes. In this paper low cost clay based support is fabricated using normal clay as the building material. It is found that the heterogeneous nucleation density of MOF crystal on ceramic supports is very low; as it is difficult to form direct chemical bonds between the surface support and the MOF material. Hence, our clay based support surface is modified by alumina coating on the surface by sol-gel technology. Boehmite sol is used for this purpose. Then Cu-BTC MOF was integrated on the alumina coated support by different techniques: *in situ* solvothermal and *step by step* seeded growth method. It has been found that with increasing the sintering temperature of the alumina coated support above 1073 K crystallinity can be increased. Increase of concentration in case of step by step seeded growth also ensures better layer of MOF impregnation over the support. Various characterizations are performed to study the nature of the MOF membrane. A detailed cost estimation of the membrane based on the cost of the raw materials is also done, and found out to be comparative with other reported ceramic membranes and far below than more popular commercially available ceramic membranes.

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γ: Surface tension of mercury

θ: Contact angle between the solid and mercury

P: Pressure difference across the mercury interface

r_p: Pore Size

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

This chapter gives an insight into the basics on membrane science and technology and highlights the chronological developments over the years. It is noteworthy to mention that the membrane science and technology is a modern unit operation which has been gaining rapid strides in various industrial applications.

1.1 Basics on Membrane

Membranes can be defined as a semipermeable barrier which restricts the transport of various chemicals in selective manner. It separates an influent stream into two effluent steams known as permeate and concentrate. Permeate is the portion which passes through the membrane whereas concentrate stream contains the portion that has been rejected by the membrane. These can be homogeneous or heterogeneous, symmetric or asymmetric in structure. These may be solid or liquid and can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be by convection or by diffusion of individual molecules. Electric field or concentration, pressure or temperature gradients are the main driving forces for membrane based separation processes. When exposed to the action of driving force it serves as a selective barrier between two phases and remains impermeable to some specific particles.

Membranes can be of various thicknesses. These can also be classified according to their pore diameter. According to IUPAC, there are three different types of pore size classifications: microporous (dp< 2 nm), mesoporous (2 nm <dp<50 nm) and macroporous (dp>50 nm) [1]. Membranes can be neutral or charged, and particles transport can be active or passive.

Passive transport can be facilitated by pressure, concentration, chemical or electrical gradients. Generally membranes can be classified into synthetic and biological membranes [2].

For various important industrial applications membrane-based separation is a viable, cost-effective, and alternative or complementary separation technology to other traditional operations such as distillation, absorption, adsorption etc.

1.1.1 Advantages of membrane based separation process

Membrane based separation methods possess some distinctive features that separate them from conventional processes. Some of the features are [3]:

i) Continuous process, no regeneration step
ii) Modular design, so suitable for scale-up
iii) Compact design for easy retrofit and integration into existing and new processes
iv) Requires less maintenance and operator attention

1.1.2 Applications

Membrane can be used effectively in variety of applications. They are summarized below [4]:

i) The small pores of the membrane can serve as a physical barrier, preventing passage of certain materials such as salt, bacteria and viruses, while allowing the free passage of water and air.
ii) The desalination of water using reverse osmosis is a well-known use of membranes as a filter.
iii) Recently, recovery from sewage and recovery of whey protein from waste stream during cheese making have been carried out with ultrafiltration and microfiltration membranes.

iv) Membranes provide a high surface area material where chemical reactions or diffusion can takes place.

v) Membranes are also used to carry out solvent extraction and catalysis.

1.2 Background of present research work

A number of attempts have been made to prepare supported-MOF membranes; starting with different methods for fabricating MOF membranes to obtaining superior performance. Workshave been reported in the past using selective nucleation and oriented growth using Self Assembled Monolayers [5].Synthesis of continuous films of Cu-BTC and MOF-5 on porous alumina support was also attempted [6, 7]. Recently, a copper-net-supported Cu-BTC membrane with high selectivity was found feasible [8]. An Improved version was developed usingseeded growth method on alumina support.A step by step procedure was devised by in-situ production of seed layer via co-ordination of H_3BTC and $Cu^{2+}$and later on the seeded support was used to grow MOF crystals on to the support [9].A reactive seeding method reported, in which porous support acted as the inorganic source reacting with organic precursor to grow a seeding layer [10]. In this project we have tried to fabricate MOF based membrane on clay based support using both direct solvothermal and step by step seeded growth followed by secondary crystal growth as the techniques for obtaining better layer of MOF on the clay based support.

1.3 Research Objectives

The research objective can be broadly divided into following sub-sections:

1) Synthesizing a MOF, i.e. Cu-BTC.
2) Synthesizing clay based support.
3) Studying the possibility to integrate MOF onto the membrane support synthesized.
4) Exploring different techniques for obtaining better layer of MOF on surface.
5) Estimating the material cost for the fabrication of membrane, based on the cost of the raw materials.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

This chapter discusses about the various types of membranes and membrane materials. A step by step procedure on ceramic membrane fabrication is also highlighted. It also gives a brief introduction on metal organic frameworks (MOFs). Recent developments in the field of ceramic membranes are also highlighted. Finally, working details of various instruments used for characterizing membrane surfaces are briefly explained.

2.1 Types of Membrane

Commonly used types of membrane are [11]:

i) Microporous membranes: This type of membrane behaves almost like a fiber filter and separates by a sieving mechanism determined by the pore diameter and particle size. Ceramics, graphite, metal oxides, polymers etc. are used in making such membranes.

ii) Homogeneous membranes: This is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be separated efficiently when their concentration differ significantly.

iii) Asymmetric membranes: An asymmetric membrane comprises a very thin skin layer on a highly porous thick structure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of the membrane materials or the pore size. The mass transport rate is determined mainly by the skin thickness. Porous sub-layer acts as support for the thin, fragile skin and has little effect on the separation characteristics.

iv) Electrically charged membranes: These are necessarily ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges, mainly used in electro dialysis.

v) Liquid membranes: It utilizes a carrier to selectively transport components such as metal ions at relatively high rate across the membrane interface.

2.2 Materials and structure of synthetic membranes

Synthetic membranes are of various types on the basis of physical structure, the materials they are made from, and in their function. These can be classified as:

1) Porous films
2) Homogeneous solid films
3) Barriers carrying electrical charges
4) Liquid or solid films containing selective carriers

Membranes come in two typical structural configurations: symmetric or asymmetric.

Materials used for the preparation of membranes are: polymer, ceramic, glass, metals and liquids [12].

2.3 Ceramic Membranes

Ceramic membrane is a permselective barrier or can be considered as a fine sieve. The performance indicators of a ceramic membrane are mainly permeability and separation factor. The main advantages of a ceramic membrane are high strength, chemical resistance, high durability and high thermal stability [13]. Selectivity of this type of membrane is based on difference in size, in diffusion coefficient, in charge, in solubility and adsorption. These are

having very high strength, which enables the use of high trans-membrane pressure. These can also be cleaned by back pulsing. Due to their chemical stability, use of chemical aggressive in cleaning method is possible steam and high temperature can be used as they are thermally stable. These membranes are very fragile in nature.

These are usually composite ones, i.e. they are consists of several layers of one or more materials. Composite membranes contain one macroporous support, one or two mesoporous intermediate layers and a microporous top layer, of several layers of one or more different ceramic materials. Commonly used materials for ceramic membranes are: Al_2O_3, TiO_2, ZrO_2, SiO_2 or combination of these materials [13].

2.3.1 Preparation

Fabrication of ceramic membrane can be done through multiple steps. First a support layer is prepared which provides mechanical strength for the membrane, followed by coating one or more intermediate layers on the support surface. Finally a dense top layer is fabricated, where separation takes place. Each step involves sintering treatment. Thus, ceramic membrane fabrications are expensive [13].

Preparation of ceramic membranes involves several steps:

(i) Formation of particle suspensions

(ii) Packing of the particles in the suspensions into a membrane precursor with a certain shape such as flat sheet, monolith or tube

(iii) Consolidation of the membrane precursor by a heat treatment at high temperatures.

Various Techniques for the preparation of ceramic membrane [13]:

i) Slip casting

It is the traditional method used in membrane preparation. In this method, a well mixed powder suspension is poured into a porous mould. Solvent in it is extracted into the pores of the mould via the capillary driving force. The slip particles are consolidated on the surface of the mould to form a layer of particle. It is important that the formation of the consolidated layer is fast so that the suspension of the particles will not penetrate into the pores of the mould. The pore size of the membrane is mainly dependent on the particle size of the powders used in the slip.

ii) Tape Casting

This is a well-known method for the production of flat sheet ceramic membranes. In this method, the powder suspension is poured into a reservoir behind a casting knife. The carrier to be cast is set in motion. The gap between the knife blade and carrier determines the thickness of the cast layer. The important variables are reservoir depth, speed of carrier and velocity of the powder suspension. Wet cast layer is passes into a drying chamber, so that a dry membrane precursor can be obtained on the surface.

iii) Pressing

It is commonly used for the preparation of disc inorganic membranes. In this, the particle consolidation into a dense layer occurs by applied force. This method is employed in screening new ionic and mixed conducting materials for development of oxygen or hydrogen permeable ceramic membranes.

iv) Extrusion

It is used for both large products ranging up to 1 ton and small products weighing few grams. In this, a stiff paste is compacted and shaped by forcing it through a nozzle. The required condition is that, the precursor should exhibit plastic behavior.

v) Sol-gel process

The main advantage of this technique is that the pore size of the membrane can be desirably controlled. There are two main routes for the preparation of membrane using this method:

a) Colloidal route- a metal salt is mixed with water to form a sol, which is coated on the membrane support to form a colloidal gel.
b) Polymer route-metal-organic precursors are mixed with organic solvent to form a sol. It is then coated on the membrane support, where it forms a polymer gel.

vi) Dip coating

The critical factors in dip coating are the viscosity of the particle suspension and the coating speed and time. Drying process starts simultaneously with the dip coating. In case of multistep process, after the complete cycle of dipping of the first layer, drying and again dipping for the second layer is repeated.

vii) Chemical vapor deposition

A layer of the same or different compound is deposited on a membrane surface through chemical reactions. Reaction takes place in a gaseous medium surrounding the component. It consists of a system of a mixture of a reactive and carrier gas, a heated reaction chamber, and a system for the disposal and treatment of exhaust gases. Gas mixture is carried to a reaction chamber and heated to a desired temperature. The products of a CVD system contain various

hazardous components and particles. Thus these are required to be treated before exhaust to the atmosphere. Reaction occurs in the vapor phase. A solid film is deposited on the surface.

2.4 Membrane Applications

Some common membrane processes are [13]

2.4.1 Gas Separation

Gas mixtures can be separated through a dense or porous ceramic membrane. Dense ceramic membranes are commonly made from crystalline ceramic materials. These allow permeation of only oxygen or hydrogen. These provide extremely high selectivity towards oxygen or hydrogen. In microporous ceramic membranes, gas permeation behaviour mainly dominated by diffusion or molecular sieving. This strongly depends on the pore size and pore size distribution of membrane, operating temperature and pressure, and the nature of the membrane and permeating molecules [13].

2.4.2 Pervaporation

It is a separation process where a liquid mixture is in direct contact with one side of the membrane, and the permeate stream is removed in the vapour state. Separation of azeotropic mixtures and heat-sensitive products are some of the applications of pervaporation [13]. As ceramic membranes have higher chemical and thermal stability than polymeric membranes, they offer more advantages for pervaporation. They do not swell and achieve a more constant performance with varying feed concentration because of better mechanical stability [13]. Gallego-Lizon et al. [13, 14, and 15] conducted experiments on pervaporation using ceramic membranes for t-butanol and iso-propanol dehydrating. They have reported that, microporous silica membranes offer the highest flux followed by zeolites, while dehydrating a 90 wt% t-

butanol solution and separation factor is highest for zeolites. Van Veen et al. [13, 16] have found that ceramic membranes show many advantages over polymeric ones, such as provide higher operation temperature, give constant operation over long period of time, and give higher flux.

2.4.3 Reverse Osmosis and Nanofiltration

These processes allow selective passage of a particular species retaining others. Main difference between RO and nanofiltration is that RO rejects all the solutes, while in nanofiltration only multivalent ions are rejected. Nanofiltration membranes show no selectivity towards monovalent ions, but RO membranes reject monovalent ions also. Currently, polymeric membranes are the only available membrane for RO and nanofiltration [13]. The major disadvantages of polymeric membranes are: excessive fouling, low resistance to chlorine and other oxidants, lack of desirable surface charge, and extensive pretreatment and waste generation [13]. Ceramic membranes provide numerable advantages over polymeric ones, such as, high thermal and chemical stability, excellent chlorine resistance, and long reliable life. These are having some disadvantages like high cost, low packing density and poor selectivity. Thus, these are not being used for commercial RO and nanofiltration operations.

2.4.4 Ultrafiltration and Microfiltration

Ultrafiltration is a process in which mainly colloidal particles or large molecular weight particles are separated through porous membrane. Based on pore size, pore size distribution, and interaction between membrane surface and solvent and solute separation takes place. Microfiltration is used for the separation of discrete particles from solution. Small insoluble particles, bacteria and yeast cells from aqueous streams are separated by this type separation process. A wide range of polymers are used for the preparation of Ultrafiltration and

Microfiltration membranes. Ceramic membranes have also been developed for these purposes. The advantages of ceramic membrane over polymeric membranes for Ultrafiltration and Microfiltration based membrane separations are: Higher chemical and thermal tolerance and can withstand harsh chemical environment.

2.4.5 Dialysis

It is basically a diffusion process. It describes the separation of substances in solution by means of their unequal diffusion rate through porous membranes. So, this can be achieved by imposing a concentration gradient across the membrane. There are so far no ceramic membranes used in dialysis.

2.5 Metal Organic Frameworks (MOFs)

Metal Organic Frameworks (MOFs) are crystalline compounds. These are mainly consists of metal ion or clusters which are coordinated to rigid organic molecules. These organic molecules act as a linker to link the metal ions. Property of the MOF depends upon the choice of the metal and the linker. They form one-, two-, or three- dimensional structures, and are porous in nature. These are having unique properties, such as highly diversified structure, large range in pore sizes, high surface areas, and specific adsorption affinity MOFs are having various applications: can be used for gas purification, gas separation, gas storage, for adsorption, as catalysts and sensors [17].

Usually MOFs are prepared under solvothermal or hydrothermal conditions. In this method substances are crystallized from high temperature aqueous solutions at high vapor pressure. This type of synthesis depends on the solubility of minerals in hot water under high pressure. Crystal growth is performed in autoclave to provide high vapor pressure. The nutrients are supplied in it along with water. A temperature gradient is maintained at the opposite ends of

the chamber. So, the hotter end dissolves the nutrients and the cooler end causes seeds to take additional growth.

Many potential uses of MOFs include gas purification, gas storage, gas separation and heterogeneous catalysis. Because of strong chemisorption that take place between electron-rich, odor-generating molecules and the framework that allows the desired gas to pass through it, MOFs are promising for gas purification. These can store molecules such as carbon dioxide, carbon monoxide, methane, and oxygen due to their high adsorption enthalpies. Gas separation can be performed as they can allow certain molecules to pass through their pores based on size and kinetic diameter. These can be used as catalysts because of their shape and size selectivity. Because of their very porous structure, mass transport in the pores is not hindered.

MOF as membrane material can be used mainly for continuous membrane-based separations, membrane reactors etc. Along with their various applications, many significant drawbacks are attached with MOFs. These are mechanically and chemically unstable, due to their nature of bonding. Some of them are prone to the formation of cracks and fractures. These are extremely sensitive to moisture. Despite of a great deal of research, there still exist some challenges to fabricate low cost, crack free, continuous MOF based membrane.

2.6 Some Recent Trends

2.6.1 For the fabrication of ceramic based membranes

Jana et al. [18] have prepared a low-cost ceramic microfiltration membrane using IIT Guwahati. They have prepared two membranes by paste casting followed by sintering at different temperatures. For one of them only clay was used while for the other one small amounts of sodium carbonate, sodium metasilicate and boric acid were added to improve the

property of the membrane. Sodium carbonate was added to create homogeneity by improving dispersion properties. Sodium metasilicate increased the mechanical strength of the membrane by the formation of silicate bonds. Boric acid gave rise to metaborates at the time of sintering, thereby increasing the mechanical strength. In their approach the materials were mixed with distilled water. The paste was casted over a gypsum surface in the shape of a circular disc. First it had been dried at room temperature for 24 hrs. and then heated at 100^{o}C for 12 hrs. For sintering they had used a programmable muffle furnace. Step by step heating was done. Sintering at the desired temperature was carried out for 6 hrs.

2.6.2For the preparation of boehmite sol

Topuz et al. [19] had prepared a stable polymeric and colloidal boehmite sol by sol-gel process through controlled hydrolysis/condensation reactions. They had reported that the structure of the sol particle was determined by the extent of hydrolysis/condensation reaction. Partial hydrolysis with a less amount of water (lesser than the stoichiometric amount) was the primary necessity for the formation of less developed nanoscale polymeric sol structures. The basic method for the preparation of stable boehmite sol had been summarized. Actually, hydrolysis of the alkoxide in excess water helped in precipitating a hydroxide and the subsequent peptization of the hydroxide with the addition of acid leading to the formation of a gel (by partial removal of the solvent) [19, 20]. Reaction temperature should be maintained above 80^{o}C to ensure the formation of boehmite. At low temperature bayerite is formed leading to an unstable sol.

It has also been reported that the phase transformation temperatures primarily determine the stability of the membranes. As thermally activated microcrack formation on membrane surface may occur due to significant structural changes above this temperature. Decrease in surface area and increase in pore size are also the results of phase transformation [19, 21].

For the preparation of colloidal boehmite sol aluminiumisopropoxide was hydrolyzed at a temperature of 90^{o}C under vigorous stirring. Predetermined amount of chelating agents were used to stabilize the products of the hydrolysis/condensation. Drop wise addition of predetermined amount of H_2O and HNO_3 was ensured [19]. From the XRD pattern they have explained that heat treatment below 800^{o}C resulted in fully amorphous structures. Huang et al. [22] have prepared an unsupported alumina membrane by sol-gel technique using aluminum isopropoxide. Changrong et al. [23] prepared a two layer ultrafiltration alumina membrane by sol-gel process using boehmite sol as precursor. The boehmite sol was prepared by hydrolysis of aluminium tri-sec-butoxide. Tri-sec-butoxide was added to distilled water. The process was carried out above 80^{o}C with constant stirring. After addition of alkoxide, dilute nitric acid was added. The resulting colloidal suspension was kept boiling until most of the alcohol had evaporated and was refluxed back to form a stable boehmite sol. The concentration of the sol was adjusted by evaporating or adding dilute nitric acid, so that the acidity can be maintained.

2.6.3 For the synthesis of MOF on different substrates

Liu et al. [7] have synthesized a continuous and well-intergrown MOF-5 membrane on a porous α-alumina substrate by in situ solvothermal synthesis.

Rajiv Ranjan et al. [24] have prepared a well-intergrown film of microporous metal organic framework by in situ growth and a seeded growth method on a porous α-alumina disc.

In Situ Growth: One side of the porous α-alumina support was polished to obtain a smoother surface for the membrane growth. This was placed inside the autoclave with the help of a Teflon holder at the time of synthesizing the MOF.

Seeded Growth of the Membrane: The polished α-alumina support was modified using polyethyleneimine (PEI) expecting that, the attachment of seeds can be enhanced via H-bonding. The PEI deposit was formed by dip-coating in a PEI-water solution followed by drying. The crystals obtained after the solvothermal synthesis of the MOF were crushed into submicrometer sized crystal. Seed layers of these particles were deposited by the manual assembly method [24, 25]. Yaoxin Hu et al. [10] have developed a reactive seeding method for the preparation of continuous MOF membranes on alumina porous supports. They have reported that the heterogeneous nucleation density of MOF crystals on ceramic supports is very low, which makes it extremely difficult to prepare defect-free MOF membranes by in situ solvothermal methods. For the preparation of integrated MOF membranes by the secondary growth method, the binding strength between the MOF crystals and supports is an important factor. But, it is difficult to form direct chemical bonds between the surface of supports and the MOF organic linkers. Thus, they have developed Reactive Seeding method, in which the support works as the inorganic source reacting with the organic precursor to grow a seed layer directly. The membrane material used in this is MIL-53. It was chosen due to its ability to form flexible MOF networks.

Jiangpu Nan et al. [9] have described a step-by-step seeding procedure for the preparation of HKUST-1 membrane on porous α-alumina support. 1mM solution of each of the Copper (II) Nitrate trihydrate and 1, 3, 5-benzenetricarboxylic acid in ethanol has been prepared. One side of the porous alumina support was polished using sand paper, and washed using abundant deionised water. Then it is dried for some time. The polished side was dipped in the following sequence:

i) First it was dipped in 1 mM1, 3, 5-benzenetricarboxylic acid and ethanol solution for 40 minutes.

ii) Then in Ethanol for 5 minutes

iii) Subsequently in 1 mM Copper (II) Nitrate trihydrate and ethanol solution for 20 minutes and finally

iv)Ethanol for 5 minutes

H_3BTC molecules were first grafted on the support surface via the covalent bond interaction between the carboxylic groups on H_3BTC and the hydroxyl groups on the alumina coated support. A portion of the carboxyl groups on H_3BTC participated in the graft first and the residual carboxylic groups bonded with Cu^{2+} during the next deposition. A Cu^{2+}ion simultaneously coordinated with two carboxyl groups enabled the growth to continue. The dipping was repeated sequentially for four cycles, followed by drying the support in oven.

2.6.4Cost of different types of membranes

Bhide et al. [26] have reported that the cost of polymeric membranes available for industrial scale operation cost around \$50-200/m^2. Often inorganic membranes are quoted to be 10 times expensive than the polymeric membranes and costs around \$500-1000/m^2 [27, 28]. Nandi et al. [27] have fabricated a stable low cost mesoporous membrane based on kaolin and other suitable low cost materials. Based on raw material cost, the membrane cost has been estimated to be \$130/m^2. Jana et al. [18] have prepared a low cost ceramic microfiltration membrane using clay and other binding materials by paste casting method: and estimated its cost to be \$19/m^2. Jana et al. [29] have fabricated a chitosan based ceramic membrane using dip coating technique. On the basis of prices of the raw material the membrane cost is found to be \$523.68/m^2.

2.7 Working Details of Various Instruments used for Characterization

2.7.1 Scanning Electron Microscope (SEM)

SEM is a type of electron microscope which provides the information about sample's surface topography, composition and other surface properties such as electrical conductivity. It images a sample by scanning it with a beam of electrons. These electrons interact with the atoms that make up sample, and produce signals which provide all the information about surface properties. The type of signal produced includes secondary electrons, back scattered electrons, characteristic X-rays, light, specimen current and transmitted electrons. Out of these, secondary electron detectors are common in SEMs. Normally the secondary electron imaging can produce very high resolution images of a sample surface. SEM micrographs yield a characteristic three-dimensional appearance of the sample surface which is useful for understanding the surface structure. When the high energy electron beam removes an inner shell electron from the sample, a higher-energy electron fills the shell and release energy. X-rays are emitted by this process, and these are used to identify the composition. It also measures the abundance of elements in the sample.

An electron beam is emitted from an electron gun, which is fitted with a tungsten filament cathode. Tungsten is used because of its highest melting point and low cost. The electron beam is condensed by one or two condenser lenses. When primary electron beam interacts with the sample, electron loses energy by repeated random scattering. The energy exchange between the electron beam and the sample, results in the reflection of high energy electrons, emission of secondary electrons and the emission of electromagnetic radiation, which can be detected, and so also the beam current absorbed by the specimen. This is used to create images of the specimen surface.

Sample Preparation: samples must be of an appropriate size to fit in the specimen chamber. These are generally mounted on a specimen holder. Specimens must also be electrically conductive and electrically grounded to prevent the accumulation of electrostatic charge at the surface. So, nonconductive specimens are coated with an ultrathin coating of electrically conducting material. Deposition of conducting material on the sample is either by low-vacuum sputter coating or by high-vacuum evaporation. Conducting materials used include gold, gold/palladium alloy, platinum etc. Metal objects require little preparation, like cleaning and mounting on specimen stub.

2.7.2 X-Ray Diffractometer

It provides information about the crystal structure, chemical composition, and physical properties of materials and thin films. This method observes the scattered intensity of an X-ray beam hitting the sample as a function of incident angle, scattered angle, polarization, and wavelength. Powdered XRD is used to characterize the crystallographic structure of powdered sample. It is also used to identify the unknown substances by comparing diffraction data against a data base.

2.7.3 Optical Microscope

Optical microscope refers to a type of microscope that uses visible light and lenses to magnify the images of samples. These images can be captured by normal light-sensitive cameras to generate micrographs. Images are captured by photographic films originally. Modern development in charge-coupled device (CCD) cameras allows the capture of digital images. Now, purely digital microscopes are available which use a CCD camera to examine a sample, so that images can be shown directly on a computer screen.

2.7.4 BET Surface Area Analyzer

BET theory explains the adsorption of gas molecules on solid surfaces. It serves as the basis for the measurement of specific surface area of a material. For the first time in 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory [30]. So, “BET” consists of the first initials of their names.

The concept used in this theory is the multilayer adsorption of molecules. Gas adsorption is the technique used for total surface area measurements. Gas molecules are condensed onto the pores of the sample. As the size of the gas molecule is known to us, the surface area of the sample can be determined. By completely covering the surface the surface area analyser can characterize the surface.

The sample has to be taken to an elevated temperature under vacuum to outgas. Nitrogen is often used because of its well established molecular size, inert nature, availability in high purity and reasonable cost. The “out gassed” sample is kept in the sample tube under high vacuum. It is immersed in a coolant bath of liquid nitrogen. The sample can attract gas molecules onto it when they are admitted to the sample tube. Depending on the amount of gas adsorbed, the resultant sample pressure is recorded. From this the surface area can be calculated.

2.7.5 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis or Thermogravimetric Analysis (TGA) is an analytic method which measures the change of weight with respect to increase in temperature in a controlled atmosphere thus to predict the thermal stability of the material tested. The primary parameters measured during analysis include weight, temperature and rate of temperature change. These data are plotted after required transformation before the results are interpreted. Based on the

interpretation, this analysis gives information on absorbed moisture, proportion of organic and inorganic materials in sample, and solvent residue apart from degradation temperature.

A typical experiment involves placing a known weight of sample in the crucible and gradually raising the temperature which can be programmed according to our requirement. The data acquisition system automatically plots the relation between temperature and weight which is finally smoothened to find the exact point of inflection. Each point of inflection may be interpreted as temperature of maximum weight loss which indirectly provides us information on its degradation.

2.7.6 Mercury Intrusion Porosimetry

Mercury Intrusion Porosimetry is method of characterization of porous media including porous powders and porous membranes. It's useful for obtaining information regarding the pore size distribution, pore radius and total porosity. Method is based on Laplace Equation which gives relationship between pressure and pore size. As mercury is a non-wetting liquid (contact angle greater than 90^{o}), equation may be modified as given below

$$\frac{2\gamma \cos\theta}{P} = r_p$$

By measuring the volume of mercury intruding into pores with respect to pressure change, the volume of each pore class in obtained.

A typical experimental procedure involves placing the sample in a special sample cup surrounding mercury. As mercury is non-wetting liquid for most surfaces, it resists entering the voids and hence pressure is applied. Pressure at which mercury enters the pore is inversely proportional to size of pore and correspondingly using the automated system, the pore size distribution and pore sizes are obtained by the experiment.

CHAPTER 3

EXPERIMENTAL WORKS

3. EXPERIMENTAL WORKS

Illustrative documentation on all the experiments performed during our study followed by various characterization steps followed to evaluate the membrane properties are clearly explained in this chapter.

A clay based support has been prepared by taking common clay using paste casting method. Sodium metasilicate, Boric acid and sodium carbonate are used as binding materials to increase the homogeneity and strength. It is sintered at very high temperature i.e. at 1123K for 3 hrs. We want to integrate our synthesized MOF onto the surface. From the SEM image it has been found that the nucleation density of MOF on bare clay support is very less as no chemical bond formation is possible between these two. Therefore, the clay based support has been coated with Alumina, which will provide free OH^- groups on the surface, by using sol gel method. Boehmite sol is used for this purpose. It is prepared by adding Aluminium tri-sec-butoxide to distilled water. The coating was done using spin coating method, i.e. adding the sol drop wise on the support while rotating the support using a rotating devise, so that uniform coating can be possible due to centrifugal force. For impregnation of MOF onto the alumina coated support two types of techniques has been adopted. First one is direct solvothermal method, in which the support is places inside the Teflon cylinder while synthesizing MOF so that some of the crystal growth will takes place on the support. The second one is the step by step seeded growth, in which first seed growth was ensured on the support through four steps and then secondary seed growth has been done using insitusolvothermal method.

Detailed cost estimation is also done based on the raw material cost. The cost is comparative with other reported ceramic membranes and far below more popular commercially available ceramic membranes.

The steps can be explained as:

3.1 Synthesis of Cu-BTC Powder

Cu-BTC was first reported by Chui et al. [31].In this paper the method reported by Hu et al. [32] is followed which is a modification of previous works by Rowsell and Yaghi [33]. 1, 3, 5-benzenetricarboxylic acid (0.266 g) was dissolved in 8 ml of a 1:1 mixture of ethanol/*N, N*-dimethyl formamide (DMF). In another flask, Copper (II) Nitrate trihydrate (1.108 g) was dissolved in 8 ml water. The two solutions were then mixed and stirred for 10 min. They were then transferred into Teflon-lined stainless steel autoclave and heated at 373 K for 10 hours. The reaction vessel was cooled to room temperature normally. The resulting blue crystals were isolated by filtration andwashed with methanol to remove impurities. The product was then dried at room temperature.

3.2 Preparation of Clay-Based Support

Soil brought was dried at 100^{o}C for 24hrs for complete removal of moisture. Then it was crushed with pestle and mortar to remove agglomerations and chucks of sand. This soil was then fed into a ball mill, crushed to fine powder and was sieved with BSS 36 mesh screen sieve to segregate coarse particles. The obtained powder was kept in an air tight container to avoid moisture and stored in a cool, dry place. Low-cost ceramic-based membrane support was prepared following the procedure described by Jana et al. [18]. The membrane was prepared by paste casting from the composition of the given materials: clay (70%), sodium carbonate (3%), Sodium metasillicate (1.5%), and Boric acid (1.5%). The materials were

mixed with distilled water (24%) and the paste was casted over analuminium foil in the shape of a circular mould of50 mm diameter and designed to have flexible thickness. After partial drying in room temperature for 24hrs, the disc was removed carefully and heated at 373K for 12h. The cast disc was heated at 1123K for 3 hrs in a furnace. Temperature of the furnace was gradually cooled to room temperature. The support was finally polished with silicon carbide abrasive paper(C-180), to give it a final shape. Sodium metasilicate increases mechanical strength by creating silicate bonds. Sodium carbonate improves dispersion properties, thereby creating homogeneity. Boric acid also increases mechanical strength by creating metaborates during sintering.

3.3 Boehmite Sol Preparation

Boehmitesol was prepared by following the procedure reported by Changrong et al. [23]. Aluminium tri-sec-butoxide was added to distilled water, which was kept above 353K and stirred thoroughly. After addition of the alkoxide, dilute nitric acid was added. The resulting colloidal suspension was kept boiling above 353K to form a stable boehmite sol. The concentration of the sol was adjusted by evaporating or adding dilute nitric acid, which was used instead of pure water in order to maintain the sol acidity. It was reported that the temperature of hydrolysis should be above353K to ensure the formation of boehmite. At lower temperature, bayerite, α-$Al(OH)_3$ forms, which cannot be peptized.

3.4 Preparation of Alumina Coated Clay Support

First dip coating procedure was applied for the coating of the Alumina sol on the clay support. The support was dipped into the sol for two times. Then drying was done for 8 hrs at room temperature followed by sintering at 1123K for 3 hrs. Effective coating has not been obtained by this method. Thus, an ultrafiltration alumina membrane was prepared by a sol-gel

process using boehmite sol as a precursor following spin coating method. A spinning setup was used to rotate the clay-support attached to it continuously at a constant speed. Boehmite sol was applied on it in drop-wise manner to obtain uniform coating using centrifugal force. The coated support was first dried at room temperature for 8h, and then sintered at 773K for 3h. From the SEM images, it has been found that the coating obtained is not uniform. XRD plot shows that the support surface was amorphous in nature. It has been reported in literature that crystalline nature of the alumina coated support can be achieved at a sintering temperature higher than 1073K [19]. Thus, the sintering temperature has been increased to 1123K.

3.5 Fabrication of MOF Membrane on Boehmite Coated Support

***In situ solvothermal method*:** This method was used to prepare well-intergrown films of microporous metal organic framework (MOF) on porous alumina coated clay-based support [7]. The synthesis gel, prepared using the procedure for Cu-BTC described in section 1, was placed in a Teflon lined stainless steel autoclave. The Boehmite coated support was placed in the autoclave with coated surface facing up. Synthesis temperature was maintained at 373K for 10h. The resulting supports with MOF film were washed with water followed by drying at 373K.

***Step-by-step seeded growth method*:**For seeded growth the procedure explained by Nan et al. [9] wasfollowed. 1mM solution of each Copper (II) Nitrate trihydrate (0.01205g) and 1, 3, 5-benzenetricarboxylic acid (0.0105g) in ethanol (50 ml) was prepared. One side of the Alumina coated support was polished using sand paper, and washed using abundant deionised water, followed by drying for some time.The polished side was dipped in sequence: First it was dipped into a solution of 1mM 1, 3, 5-benzenetricarboxylic acid and ethanol for 40 minutes followed by dipping in ethanol solvent for another 5 minutes. The support was

then transferred into a solution of 1mM Copper (II) Nitrate trihydrate and ethanol solution for another 20 minutes and finally once again dipped into ethanol solvent for another 5 minutes.

The dipping was repeated sequentially for four cycles. Then the seeded support was dried in oven. The coordinatively synthesized support was kept in the autoclave similar to that of in-situ solvothermal method for the secondary growth of crystal in the seeded support. We also studied step by step growth of MOF crystals using 10mM ethanolic solution of 1, 3, 5-benzenetricarboxylic acid and Copper (II) Nitrate trihydrate following similar procedure.

3.6Characterization

Characterization was performed using SEM, Powder XRD, TGA, BET surface area analyzer and Mercury porosimetry. The membrane morphologies were observed via scanning electron microscopy (SEM, JEOL JSM-6480 LV)equipped with an energy dispersive X-ray spectrometer (EDX). Prior to imaging, each sample was platinum coated in a specialized device to increase the conductivity for a better imaging. The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite monochromatized CuKα radiation(λ=1.5406Å) in 2θ angles ranging from 5^{o} to 75^{o} with a step size of 2 degree and scanning rate 1 minute.BET surface area analysis was performed by BET surface area analyzer (Autosorb-1, Quantachrome). The relative pressure in BET surface area calculation was between 0.05-0.35. Finally, thermal analyses of samples were carried out in detail in a TGA apparatus, SHIMADZU (DTG 60 H). 60 µl alumina crucibles were used during TGA analysis. The different ceramic membranes and supports were analyzed by comparing images taken in an optical microscope (Hund Wetzlar H600). The pore size distribution and total porosity of the membrane sample was determined using Mercury Intrusion Porosimeter (QuantachromePoremaster 32).

CHAPTER 4

RESULTS & DISCUSSIONS

4. RESULTS AND DISCUSSION

This chapter elaborates all our experimental findings during our course of study. Each and every aspect of our research output is aptly highlighted in this section.

4.1 Results on Cu-BTC Synthesis

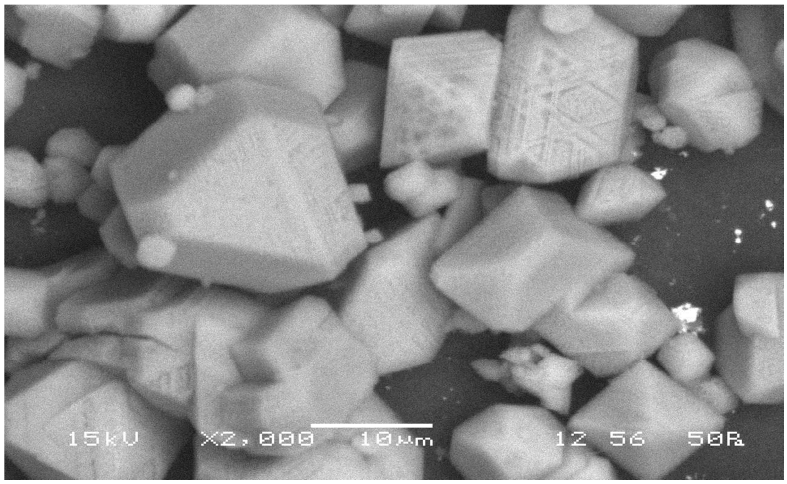


Figure 1: SEM image of Cu-BTC Sample

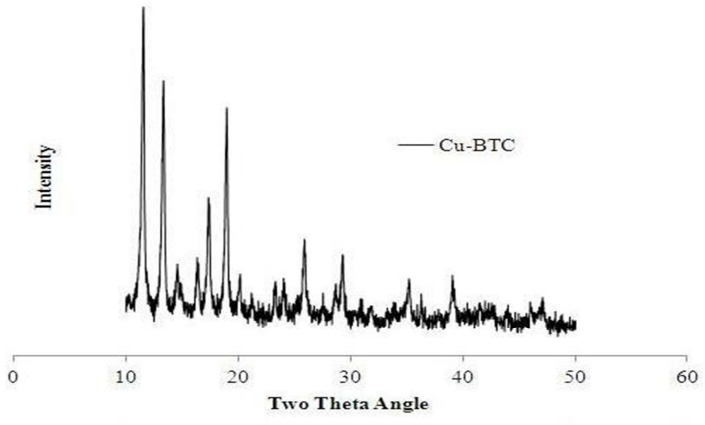


Figure2: Powder X ray diffraction pattern of Cu-BTC Sample

The powdered XRD pattern and the SEM images of Cu-BTC synthesized matches the Cu-BTC pattern reported in literature. Clearly from the SEM image its shape can be seen as octahedral in shape. XRD patterns show clearly the crystalline nature of the products formed. The peaks formed at 11^{o}, 13^{o}, 14^{o} and $17^{o}$are characteristic peak of Cu BTC according to literature and well corresponds to our data too, confirming the formation of Cu-BTC [32].

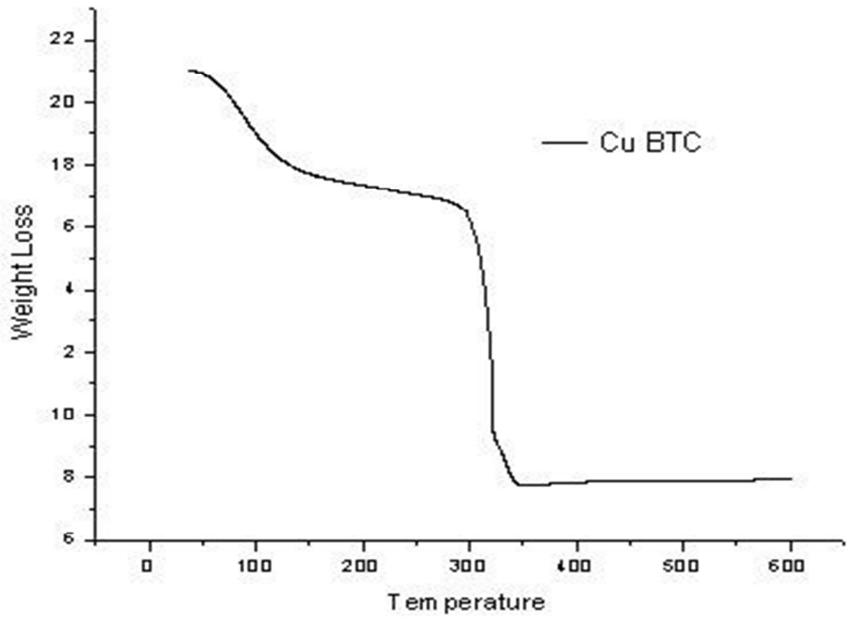


Figure 3: Thermo Gravimetric Analysis of as-synthesized Cu-BTC sample

This typical TGA profile shows three distinct weight loss steps. In the temperature range of 25-125^{o}C the weight loss is purely due to removal of moisture and trapped methanol. The second step from 125^{o}C to 275^{o}C is a horizontal plateau, where the weight remains fairly constant. Beyond 275^{o}C the structure collapses.

4.2 MOF based Ceramic Membrane

4.2.1 Surface Morphology of MOF Membranes

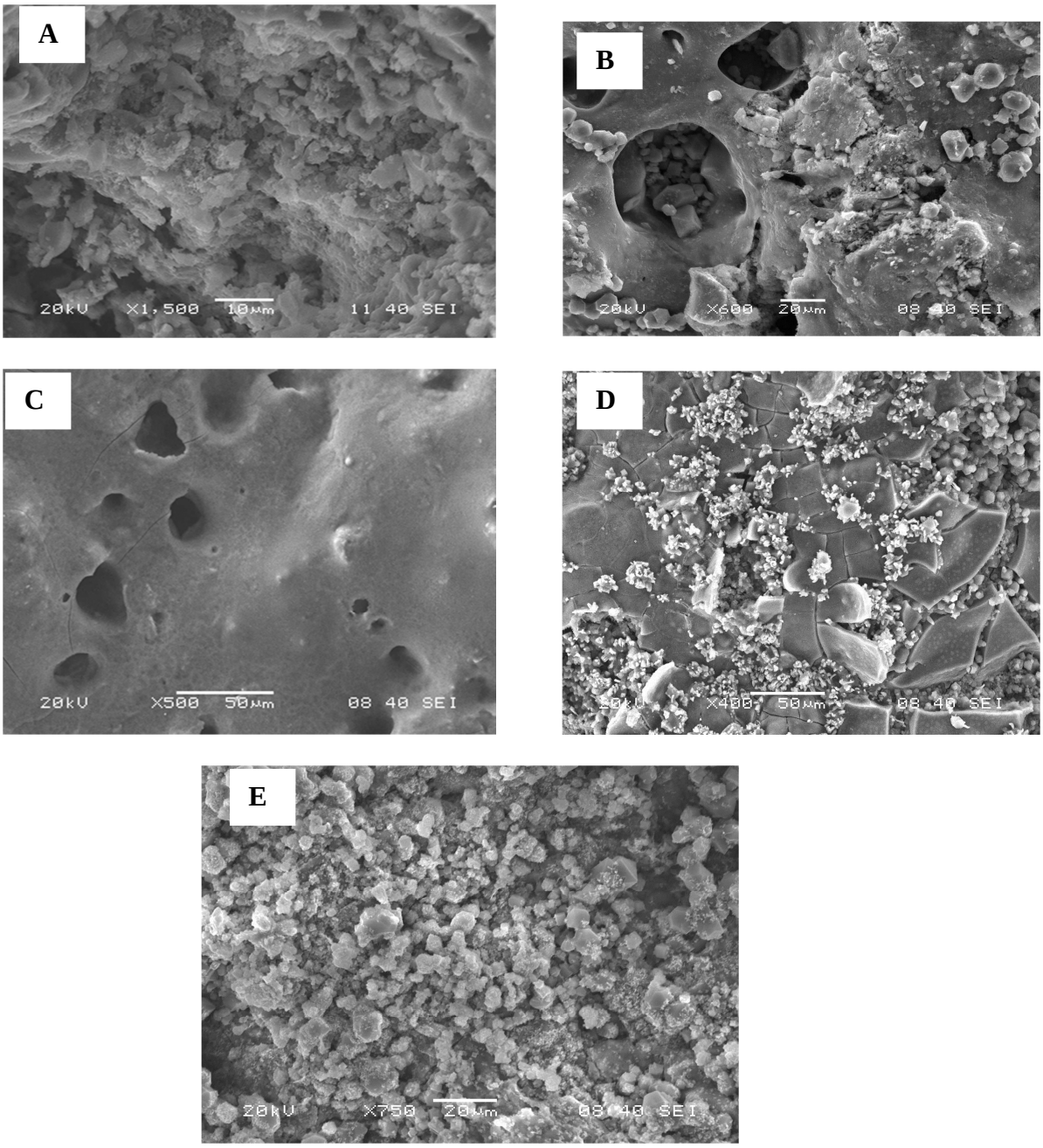


Figure 4: SEM Images of: (**A**) Clay-Based Support (**B**) MOF growth on bare clay base support (**C**) Alumina Coated Support sintered at 773 K (**D**) Directly synthesized MOF based membrane sintered at 773 K**(E)** Directly Synthesized MOF based Membrane Sintered at 1123 K

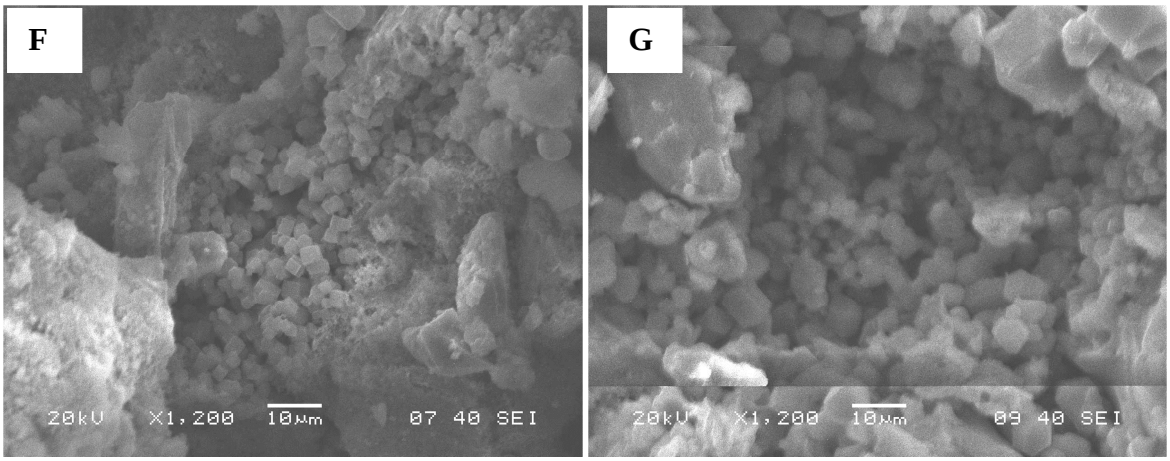


Figure 5: SEM Images of :**(F)** Step by Step fabrication of MOF Membrane using 1 mM solution and sintered at 1123 K, and **(G)** Step by Step fabrication of MOF Membrane using 10mM solution and Sintered at 1123 K.

From the SEM images (Figure 4.4 **A**), the porous nature of bare clay support can be clearly established. It is observed from (Figure 4.4 **B**) that the nucleation density of MOF directly on clay based support is very low. This may be due to the inability of MOF precursors from the solution to form direct chemical bonds with the support. These observations led us to treating the surface with alumina which can provide better activated surface which can aid in increasing the coverage of MOF crystals.

MOF crystal growth on alumina coated support which was sintered at 773 K is highly non-uniform (Figure 4.4 **D**) while that sintered at 1123 K is uniform (Figure 4.4 **E**)and nucleation density in this case is better (Both solvothermal and step by step growth). The experimental results of step by step synthesis using two different concentration doesn't yield much significant increase in coverage but upon comparing the SEM images, a significant size difference of crystals is found. Reasons may be attributed to easier formation of crystal seeds in concentrated synthesis solution than less concentrated one.

4.2.2 Optical Microscopy for seeded supports

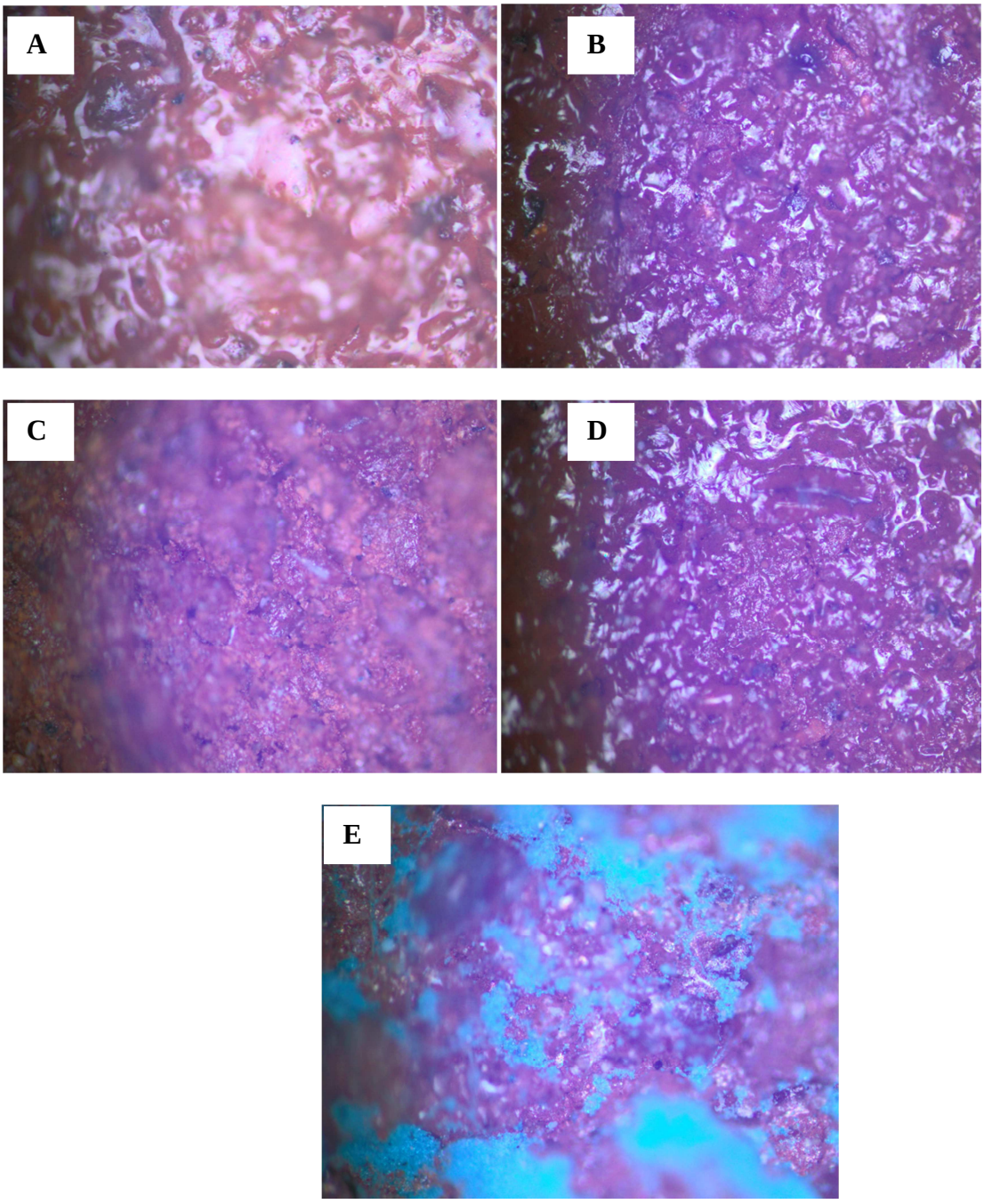


Figure 6: Optical microscopy images of MOF based membrane (1mM) after different cycles with resolutions of the images is shown in the bracket (**A**) 1st Cycle (20 X) (**B**) 2nd Cycle (10 X) (**C**) 3rd Cycle (10 X) (**D**) 4th Cycle (10 X) (**E**) After solvothermal synthesis (10 X).

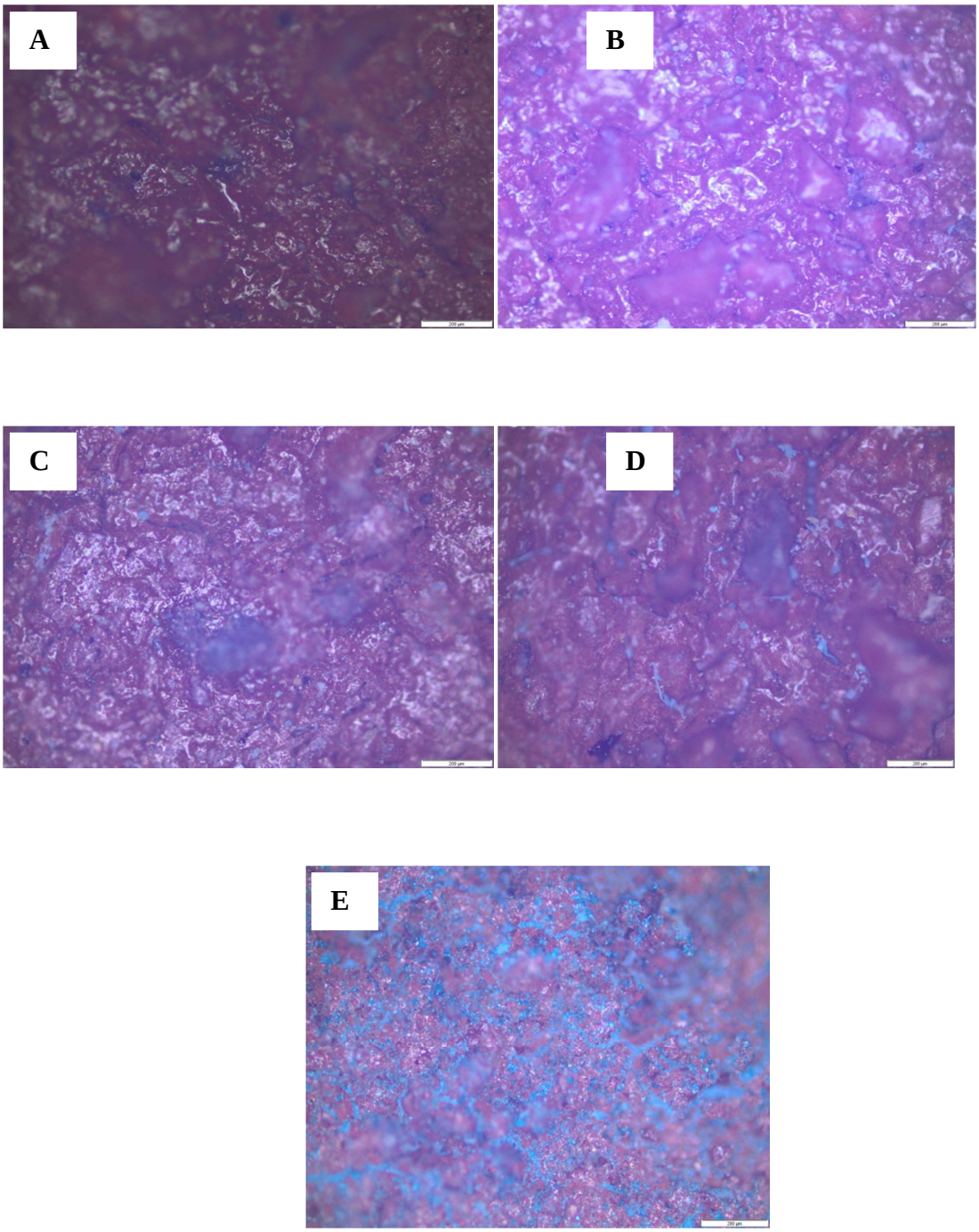
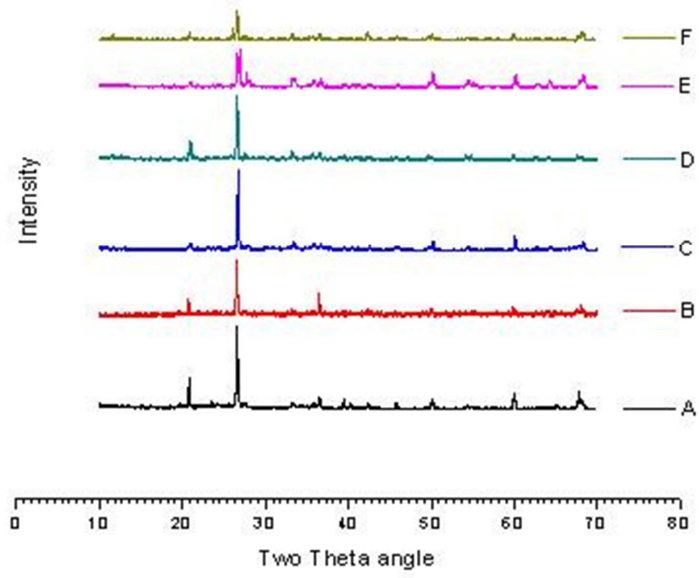


Figure 7: Optical microscopy images of MOF based membrane (10mM) after different cycles with resolutions of the images is shown in the bracket (**A**) 1st Cycle (20 X) (**B**) 2nd Cycle (10 X) (**C**) 3rd Cycle (10 X) (**D**) 4th Cycle (10 X) (**E**) After solvothermal synthesis (10 X).

Optical microscopy images establish the effectiveness of each of cyclic operation for seed growth in step by step fashion. From these images (Figure 4.6 and Figure 4.7) it has been confirmed that the seed growth on the support increases with increase in number of cycle. Upon completion of third cycle, blue color is observed at the surface and pores of support which indicate the formation of seeds and complete crystal growth is accomplished after the solvothermal synthesis.

The imaging for 1st cycle had to be performed at higher resolution (20 X) because of the very low density of seed growth whereas all other samples were imaged at 10 X resolution. We assumed that better seed growth may be obtained if the concentration of the seeding solution is increased and hence same technique repeated at 10 mM concentration. In agreement with the assumption, the increased crystal density formed in higher concentration is evident from the optical images as shown above (Figure 4.6 **E** and Figure 4.7 **E**).

4.2.3 XRD Pattern for MOF based Membrane



F- Seeded Growth MOF Membrane (10 mM)

E- Seeded Growth MOF Membrane (1 mM)

D-Solvothermal MOF Membrane

C-Alumina Coated Support (1123 K)

B-Alumina Coated Support (873 K)

A-Clay Based Support

Figure 8: Powder XRD patterns of Clay Support, Alumina Coated Support and MOF Membranes.

Figure 4 7 shows and explains the XRD patterns of synthesized support and membranes. The peaks of normal clay support indicate quartz which is constituent of clay (Figure 4.8 **A**) and it's carried further to all the XRD patterns. On comparing patterns of alumina coated support sintered at 873 K and 1123 K (Figure 4.8 **B** and Figure 4.8 **C**), the amorphous nature of support sintered at 873 K is clearly distinguished from crystalline nature of support sintered at 1123 K. Direct solvothermal and step by step growth techniques for MOF membrane synthesis on alumina coated clay support shows distinct Cu-BTC peaks due to larger crystal density (Figure 4.8 **D**, Figure 4.8 **E** and Figure 4.8 **F**) and it well corroborates with the major peak of Cu-BTC. Thus XRD profile serves as an additional evidence of Cu-BTC on support.

4.2.4 BET Surface Area Analysis

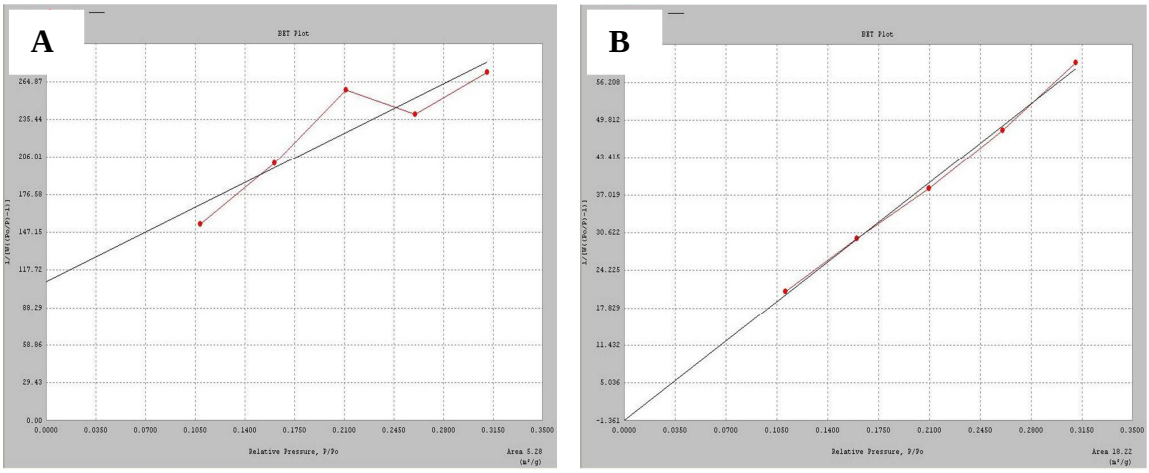


Figure 9: BET Surface Area Plot of (A) Bare Clay Support and (B) MOF Membrane

BET surface area analysis showed an overall improvement in surface characteristics. Actually, the surface area has been increased from 5.28 m^2/g of bare clay based support to 18.22 m^2/g of MOF based membrane prepared solvothermally on alumina coated support sintered at 773 K. This increase in surface area is largely due to contribution from the MOF coat present on the surface. Additionally, a closer look at the isotherm profiles gives good information on the pore sizes. Since BET isotherm data is valid within a relative pressure

between 0.05-0.35, the isotherm data is shown within this stipulated range. In case of bare clay support, we can see formation of an inflection point (Figure 4.8) around a relative pressure of ~0.2. This inflection is due to the formation multiple layers during N_2 adsorption analysis at cryogenic conditions indicating presence of mesopores. Tuning of bare clay surface with boehmite sol followed by impregnation of Cu-BTC into it reduces the pore sizes considerably and that limits the pore sizes (Figure 4.8).

4.2.5 Mercury Porosimetry of clay support

Mercury Porosimetry analysis gives us information about the pore size distribution of the synthesized membranes and the total porosity of the membrane.

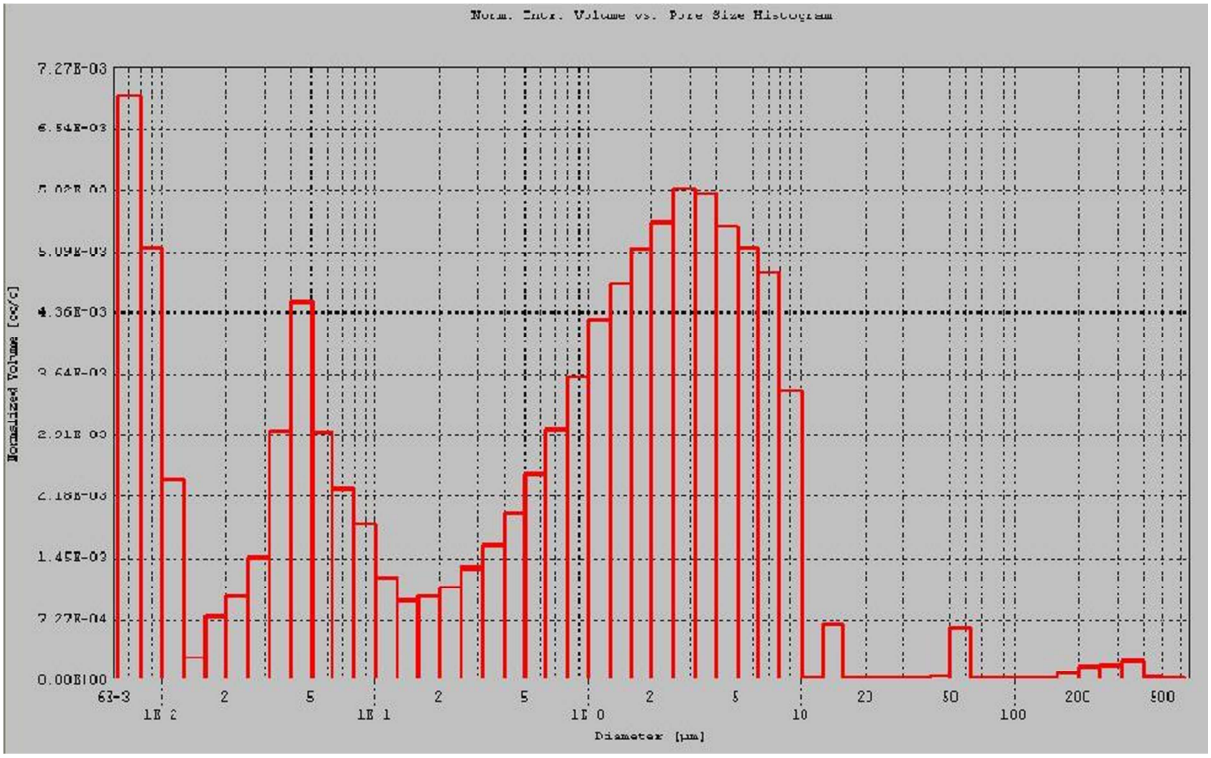


Figure 10: Histogram of Volume of Hg Intruded Vs Diameter of pore

The pore size distribution of the membrane sample is obtained by plotting a histogram of volume of Hg intruded Vs. diameter of the pore. In Figure 4.10, each vertical bar represents the volume occupied by particular pore size range in the total sample volume. We can also

observe that maximum volume is occupied by the pores, which ranges from 1 µm to 5 µm, even though there is also a significant presence of pores below 1 µm range. The presence of macro pores larger than 10 µm is quite scantly as evident from the little volume occupied.

The total porosity of the membrane obtained by Hg intrusion is 17.6968 %. This is quite appreciable for a membrane sample considering that it should give a reasonable flux for permeation experiments.

4.2.6. TGA of Clay Support and MOF Membrane

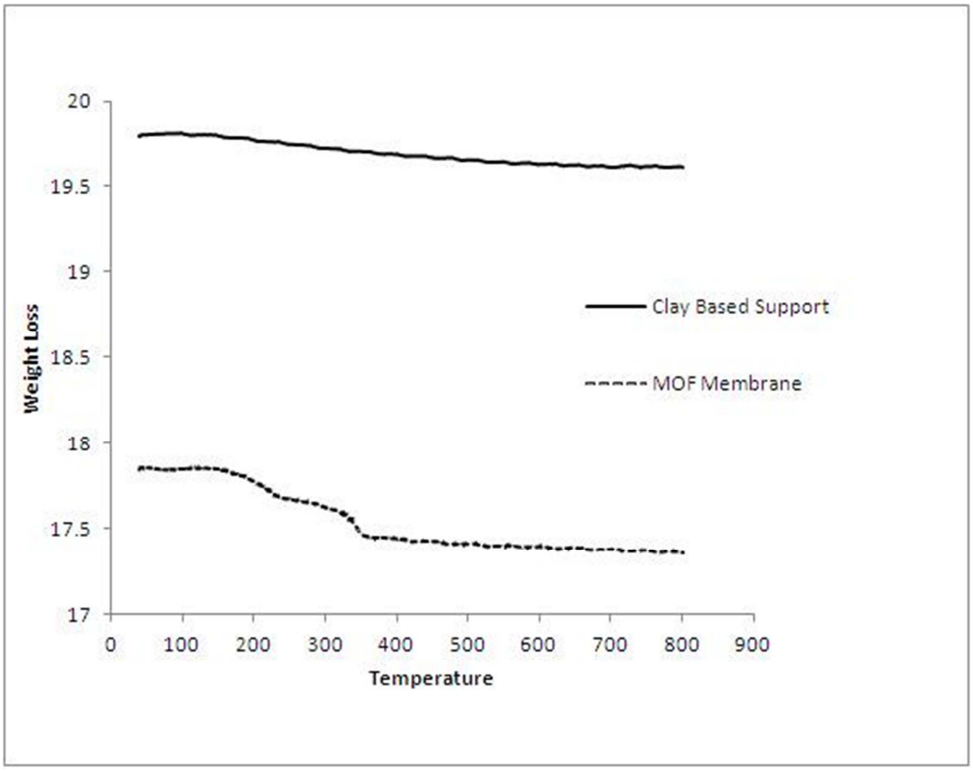


Figure 11: TGA Profile of Clay Support and MOF Membrane

Figure 4.11 shows the TGA pattern for both clay support used for fabrication of membrane and the MOF membrane. The very narrow weight loss seen in support partly due to removal of moisture (temperature up to 100^{o}C) and the carbon dioxide generated upon oxidizing

calcium carbonate (540-760^{o} C). The TGA also establishes that there is no major weight loss upon sintering the membranes to high temperatures.

TGA profile of MOF membrane may be divided into four zones of weight loss. Initial zone, i.e. 40^{o}C to 100^{o}C is mainly due to removal of surface moisture. In the temperature range of 150^{o}C to 250^{o}C, the weight loss observed is partly due to removal of moisture present in the pores of membrane and start of MOF degradation. The rapid degradation of MOF is observed between 250^{o}C and 350^{o}C which is the maximum temperature of stability of Cu BTC MOF as shown in Figure 4.3. Again, the weight loss for region greater than 350^{o}C is mainly due to degradation of calcium carbonate to carbon dioxide.

4.2.7. Estimation of material cost of the membrane

For alumina coated support

The material cost of the solvothermally fabricated membrane is calculated in terms of Rupees per square meter. 40gms of clay has been taken in addition with the other materials in their respective composition as described in Somen Jana et al. [14]. From this total 21 alumina coated supports are fabricated. Diameter and thickness of each sample has been measured using verniercalliper. Total surface area of each sample was calculated assuming them cylindrical in shape. The purchasing cost of each chemical in rupees per gram was known. From this material cost of the required chemicals can be determined. Dividing this cost with total surface area of sample prepared we can get the material cost for fabrication of alumina coated support in rupees per square meter.

Materials used with their cost

Name of the material	**Cost (rupees/gram or ml)**	**Amount required (gm or ml)**	**Total cost (rupees)**
Clay	-	28	-
Water	-	9.6	-
Sodium metasilicate (LobaChemie)	0.644	0.6	0.3864
Boric acid (RANKEM)	0.9	0.6	0.54
Sodium carbonate (MERCK)	0.432	1.2	0.5184
Aluminium tri sec-butoxide (Fluka)	12	5.47	65.64
Nitric acid (RANKEM)	0.48	6.95	3.336
Total cost			**70.4208**

Table 1: Cost of Raw Materials Used for the Fabrication of Alumina Coated Support

Area calculation

Sample	**Diameter (cm)**	**Thickness (cm)**	**Total surface area (sq. cm)**
1	1.86	0.5	8.352
2	1.87	0.46	8.19
3	1.2	0.26	3.24
4	1.19	0.28	3.27
5	1.2	0.28	3.32
6	1.2	0.28	3.32
7	1.2	0.28	3.32
8	1.2	0.28	3.32
9	1.2	0.26	3.24
10	1.18	0.23	3.04
11	1.18	0.24	3.08
12	1.19	0.25	3.16
13	1.2	0.27	3.28
14	1.86	0.45	8.06
15	1.29	0.48	4.56
16	1.37	0.49	5.05
17	1.35	0.5	4.98
18	1.30	0.46	4.53
19	1.0	0.5	3.14
20	0.98	0.5	3.05
21	1.0	0.49	3.12
TOTAL			**88.622**

Table2: Calculation of Total Surface Area of Sample Prepared

So, material cost per unit area is 7940 rupees per square meter for the fabrication of alumina coated support.

For MOF crystal growth on alumina coated support

One support having area of 16.542 cm^2, has been placed inside the Teflon cylinder for the growth of crystal solvothermally. Cost of materials required for the synthesis of membrane can be done as above.

Name of the material	**Cost (rupees/gram or ml)**	**Amount required (gm or ml)**	**Total cost (rupees)**
Ethanol (Changshu yangyuan)	1	4	4
DMF(Changshu yangyuan)	0.5	4	2
H_3BTC (MERCK)	7.848	0.266	2.087
Cu $(NO_3)_2$ (MERCK)	1.4688	1.108	1.627
Water	-	8	-
TOTAL			**9.714**

Table 3: Cost of Raw Materials Used for the Fabrication of MOF Membrane on Alumina Coated Support

Cost for crystal growth on alumina coated support is 5870 rupees per square meter.

Total cost of the MOF based membrane is estimated to be Rs13,810 /m^2 on the basis of the cost of the raw materials used.It is comparative with other reported ceramic membranes and far below more popular commercially available ceramic membranes.

CHAPTER 5

CONCLUSIONS

& FUTURE WORKS

5.CONCLUSIONS& FUTURE WORKS

Synthesis and characterization of MOF based membrane using low cost clay based support has been successfully carried out in our present study. Different techniques for the integration of MOF on the support surface have also been carried out. Cost analysis also showed that the membrane fabricated is cheaper than commercially available ceramic membranes and compare well with other reported cost data.

As a continuation of this present study, many works have already been initiated in the lab. The effectiveness of the membrane can be truly judged from the permeation study and the subsequent liquid based separation applications in micro and ultra-filtration range. Apart from Cu-BTC, the deposition of Cr and Zn based MOFs can also be studied, specific to other applications. Gas separation (especially H_2) would be a sophisticated venture using MOF based ceramic membranes and work can be initiated in this direction.

CHAPTER 6

REFERENCES

6.REFERENCES

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CHAPTER 7

APPENDICES

7.1. Appendix-I: Variation of XRD peaks of alumina coated support with temperature

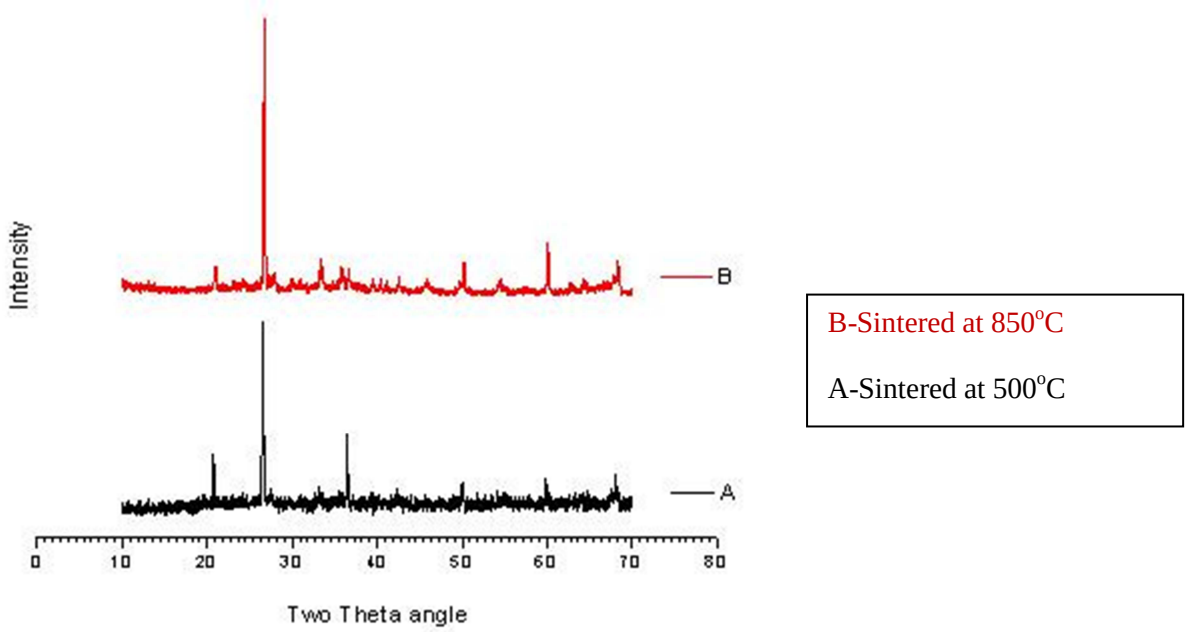

Figure 12: Variation of XRD peaks of alumina coated support with temperature

Ascan be seen from the XRD peaks of the alumina coated support with increasing temperature, the surface is becoming more crystalline in nature. The support sintered at 500°C is showing amorphous character. The peaks we are getting is due to the crystalline nature of the clay support. So, it has been confirmed that above 800°C sintering temperature the surface becomes crystalline in nature.

7.2. Appendix-II: Variation of XRD peaks of MOF based membrane with technique

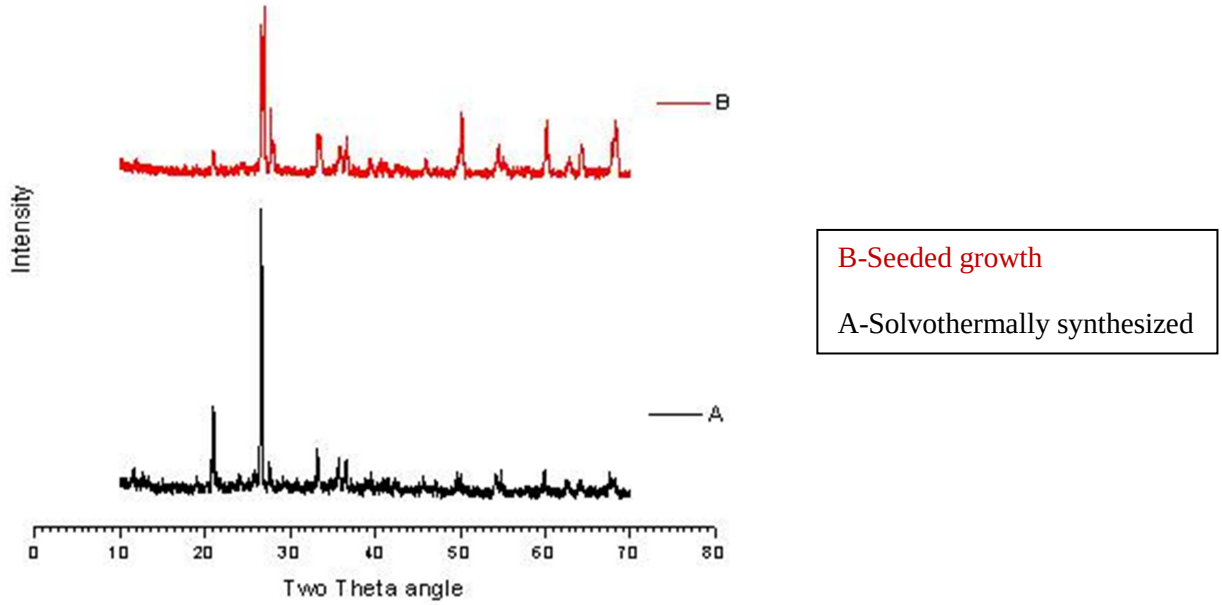

Figure 13: Variation of XRD peaks of MOF based membrane with technique

In both the peaks of the MOF membrane MOF crystal formation can be ensured by the formation of the characteristic peaks of the Cu-BTC. In case of solvothermal process the intensity of the peaks due to MOF is higher than that of seeded growth but the peak due to quartz is decreased. This may be explained as the crystal growth is more uniform in case of seeded growth, while more crystals are formed in case of direct solvothermal method.

7.3. Appendix-III: Variation of XRD peaks of MOF based membrane with concentration

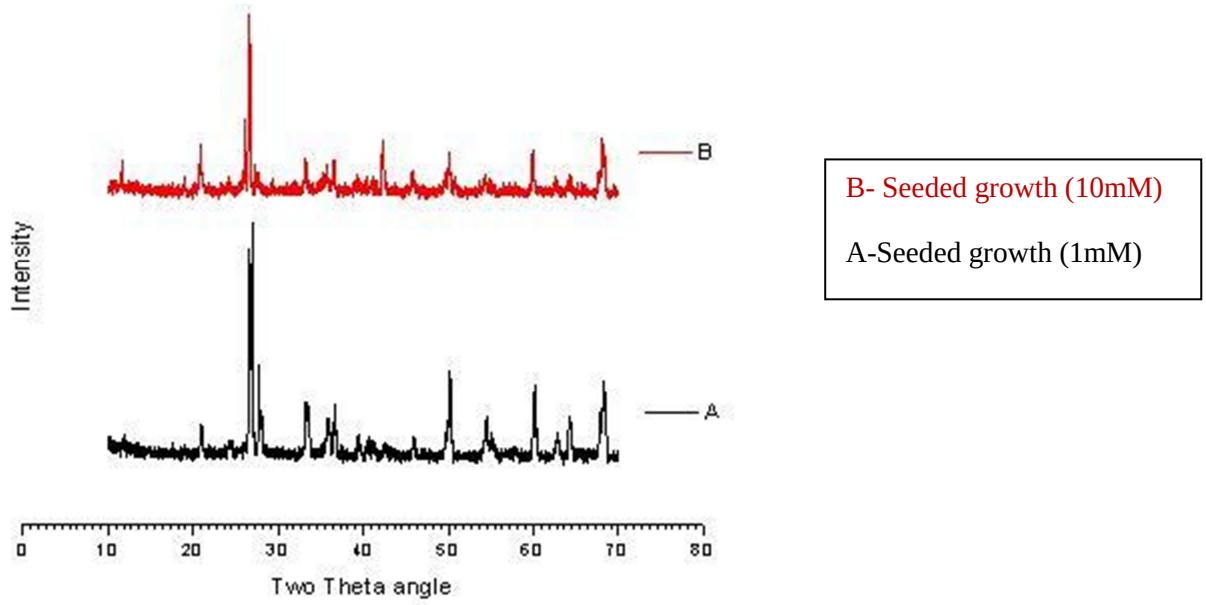

Figure 14: Variation of XRD peaks of MOF based membrane with concentration

From the peaks it can be observed that with increasing concentration in case of seeded growth intensity of MOF crystal formation increases as well as peak due to quartz decreases. This may be due to increase in uniformity and amount of MOF crystal formation.